

Infrared spectroscopy on the fullerene C₇₀ under pressure

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1 Introduction C₇₀ is the most commonly occurring higher order fullerene next to C₆₀. The C₇₀ molecule has a slightly elongated "rugby ball" shape with molecular symmetry D_{5h} . At room temperature and ambient pressure, the crystalline C₇₀ generally has a face-centered-cubic (fcc) or rhombohedral (rh) structure and exists in the first orientationally-ordered state [1]. In this ordered state, the rotation of the C₇₀ molecules is restricted to that around the long axis of the molecules [2,3].

Several experimental investigations under pressure have been performed on this compound. Generally, compression of the lattice forces the C₇₀ molecules to line up in parallel, inducing and enhancing the orientational ordering of the molecules, hence leading to a rh symmetry of the lattice [1]. This structural phase transition, where the crystal symmetry changes from fcc to rh, was studied by X-ray diffraction measurements. A first-order transition below 0.9 GPa at RT was reported by Kawamura *et al.* [4–6]. The rhombohedral distortion was found to increase with increasing pressure, with a saturation of the rhombohedral angle at around 1 GPa; this saturation was attributed to the transformation to a monoclinic (mc) phase [5]. Christides *et al.* suggested that the onset of the fcc-rh transition occurs around 0.35 GPa, with the fcc phase coexisting up to 1 GPa at RT, based on their energy dispersive X-ray diffraction studies [7].

Furthermore, thermal conductivity and compressibility studies on C₇₀ found two anomalies at around 0.15 GPa and 0.7 GPa at 296 K [8–10]. These anomalies were attributed to a continuous change of the orientational ordering and eventual "freezing" of molecular rotations probably accompanied by a fcc-rh structural phase transition, in analogy to the changes observed upon decreasing temperature.

Also, a few pressure-dependent Raman and infrared spectroscopic studies were performed on C₇₀ at RT. However, some of these investigations used mixtures of C₆₀ and C₇₀ which is undesirable as the presence of C₆₀ influences the physical properties of C₇₀ [11, 12]. The pressure-dependent Raman spectroscopic measurements on pure C₇₀ found anomalies which could be attributed to the orientational ordering transitions [13–15]. Sood *et al.* found an anomaly at around 1 GPa in the pressure-dependence of the frequencies and linewidths of the Raman-active vibrational modes which was attributed to the fcc-to-rh orientational ordering transition [15]. Raman studies by Maksimov and coworkers exhibited two anomalies at around ≈ 2 GPa and ≈ 5.5 GPa, which were attributed to the signatures of the orientational ordering of C₇₀ molecules [13, 14]. The pressure-dependent infrared study on mixtures of C₆₀ and C₇₀ found no discontinuous change apart from the splitting of a vibrational mode at 535 cm^{-1} [16]. Further-

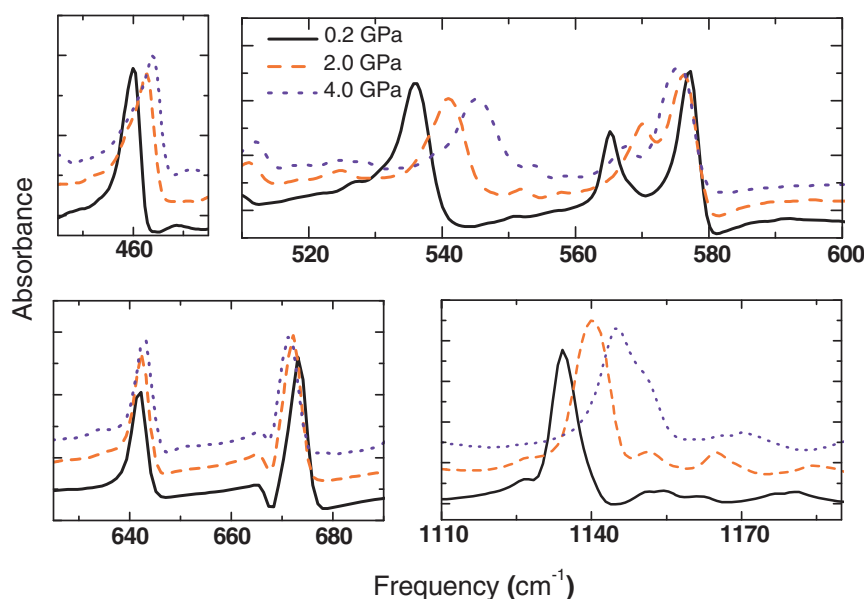


Figure 1 Infrared absorbance spectra of C_{70} as a function of pressure. The pressure dependence of selected vibrational modes are shown for few pressures.

more, infrared measurements on pure C_{70} found no discontinuous change in the pressure dependence of the vibrational modes [17].

Thus, various pressure-dependent spectroscopic measurements exhibit discrepancies in the reported anomalies. Despite these controversial results from optical investigations, a tentative, low-pressure phase diagram [1] is accepted by now, which shows a change of the orientational ordering of the C_{70} molecules induced at around 1 GPa. Related to the change in orientational order is a change in the crystal symmetry to rh.

The aim of our work was to clarify the discrepancies in the optical response of C_{70} under pressure and confirm the tentative low-pressure phase diagram [1].

2 Experiment The experiments were carried out on high-purity (> 99%) C_{70} powder samples, with an fcc phase at ambient conditions according to infrared studies showing phase transitions at 280 and 340 K (the admixture of another fullerene with C_{70} should lead to shifts of the lattice parameters and transition temperatures [18,19]). The pressure-dependent transmittance measurements were performed at room temperature using a Bruker IFS 66v/S spectrometer with an infrared microscope (Bruker IRscopeII). The pressure was generated by a diamond anvil cell (DAC) of Syassen-Holzapfel type [20] and the ruby luminescence method was used for pressure determination, with an accuracy of 0.1 GPa [21]. The pressure-dependent transmittance was studied for pressures up to 4 GPa in the infrared frequency range (400 cm^{-1} - 8000 cm^{-1}). The transmittance and the corresponding absorbance of C_{70} was obtained in the following way: The intensity $I_s(\omega)$ of the radiation transmitted by the mixture of powder sample and the pressure transmitting medium (CsI) was measured. As ref-

erence, the intensity $I_r(\omega)$ transmitted by the pure pressure transmitting medium inside the DAC was used. The transmittance was then calculated according to $T(\omega) = I_s(\omega)/I_r(\omega)$. The absorbance was calculated as $A = \log_{10}(1/T)$.

3 Results and discussion C_{70} has D_{5h} symmetry with the vibrational modes $10A_2'' + 21E_1' + 12A_1' + 22E_2' + 19E_2'' + 9A_2' + 9A_1'' + 20E_2''$, where only the E_1' and the A_2'' modes are infrared-active [22–24]. In our transmittance measurements we observed nearly 20 infrared active modes; some of them have very low intensity. The pressure-dependent absorbance spectra of selected vibrational modes of C_{70} are shown for few pressures in Fig. 1. With increasing pressure, most of the vibrational modes of C_{70} shift to higher frequencies, except the modes at around 577 cm^{-1} , 673 cm^{-1} , 727 cm^{-1} , 742 cm^{-1} and 795 cm^{-1} . The redshift of the vibrational modes 577 cm^{-1} , 673 cm^{-1} and 795 cm^{-1} with increasing pressure was also observed in the earlier infrared studies under pressure [16,17]. Although the intensity of some vibrational modes decrease with increasing pressure, most of the vibrational modes persist up to 4 GPa. Furthermore, we do not find signatures of new vibrational modes and mode splittings up to 4 GPa [25].

The detailed quantitative information on the pressure dependence of the vibrational modes of C_{70} can be extracted by fitting with Lorentzian functions. Such a fit allows the accurate determination of the frequencies of the vibrational modes with an accuracy of $\pm 0.2\text{ cm}^{-1}$. The extracted frequencies are shown in Fig. 2 as a function of pressure below 3.5 GPa. The pressure dependence of the vibrational modes of C_{70} is nearly linear except for an anomaly at around 0.8 GPa. This anomaly, observable for all vibrational modes, is not sharp but appears to be slug-

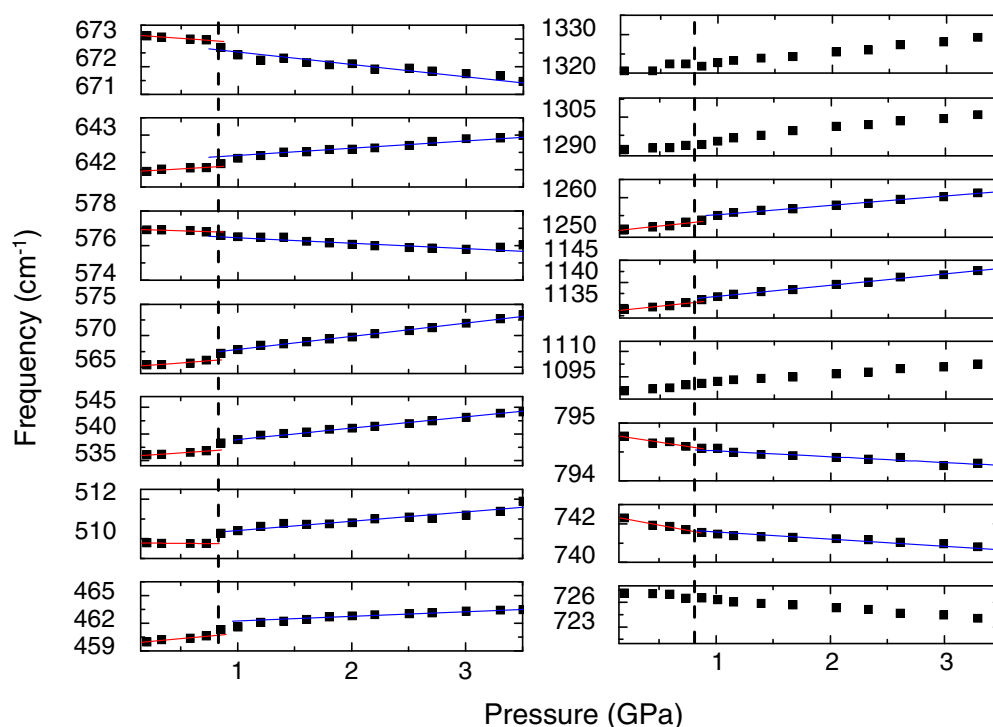


Figure 2 Pressure-dependent frequencies of the vibrational modes of C_{70} in the pressure regime $p < 3.5$ GPa. The vertical dashed line indicates the pressure of the orientational ordering phase transition. The solid lines represent the linear fits of the pressure dependence of the vibrational modes showing a clear change in the pressure-induced shifts, for the pressures below and above the transition pressure.

gish: For example, the mode at 460 cm^{-1} starts to deviate from a linear dependence at 0.7 GPa and follows a linear increase with a different slope above ≈ 1.2 GPa.

Further confirmation of the anomaly can be obtained by checking for a maximum in the pressure derivative ($d\nu/dp$) of the frequency of the vibrational modes. Figure 3 shows as examples the pressure derivative for the modes at 535 cm^{-1} and 565 cm^{-1} as a function of pressure. A broad maximum centered around 0.8 GPa is observed in the pressure derivative plot, clearly indicating the anomaly in the pressure dependence of the vibrational modes.

Our results obtained with small pressure steps indicate that an anomaly at around 0.8 GPa indeed exists in the pressure dependence of the infrared-active vibrational modes. The pressure coefficients ($d\nu/dp$) of various modes below and above the critical pressure are listed for both pressure regimes in Table 1. These pressure coefficients though slightly different from previous works, lie in the same range [17]. The change in the pressure coefficient of the vibrational modes at around 0.8 GPa is a clear sign for a phase transition and can be attributed to an orientational ordering transition, where the uniaxial motion of C_{70} molecules stops and the molecules are ordered. This transition is probably accompanied by a structural change from fcc to rh or mc phase.

The pressure of the ordering transition (0.8 GPa) is close to the value (1 GPa) reported in the Raman studies by Sood *et al.* [15]. The slow change in the pressure dependence of the vibrational modes, is similar to the pressure-response observed in energy dispersive X-ray and thermal conductivity studies [7, 10]. This sluggish character of the transition could be due to a continuous change of the orientational order. An alternative explanation could be the coexistence of two phases (fcc, rh) of solid C_{70} in the transition pressure regime, causing a sluggish response regarding pressure (or temperature).

4 Conclusion We presented pressure-dependent infrared transmittance measurements on fullerene C_{70} at room temperature in the pressure range up to 4 GPa. The vibrational modes of C_{70} exhibit a nearly linear pressure dependence with a sluggish anomaly at around 0.8 GPa. This anomaly observed for the first time in the infrared spectroscopic measurements could be attributed to the orientational ordering phase transition of C_{70} molecules. The sluggish behavior could be either due to a continuous change of the orientational order or due to the coexistence of two phases in solid C_{70} .

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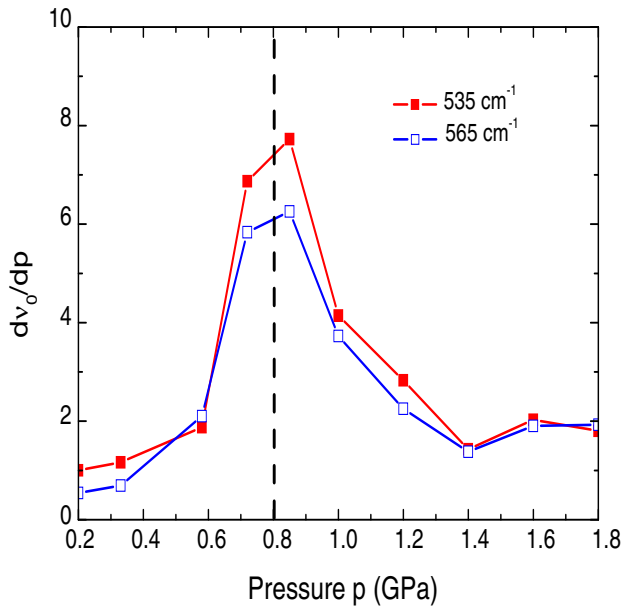


Figure 3 Pressure derivative of the frequency of selected vibrational modes at 535 cm^{-1} and 565 cm^{-1} as a function of pressure. The broad anomaly around 0.8 GPa is clearly revealed by the maximum in the pressure derivative of the frequency of the vibrational modes.

Table 1 The pressure coefficients dv/dp of the vibrational modes are tabulated for the pressure regimes below and above the critical pressure ($p \approx 0.8$ GPa).

Mode frequency (cm^{-1})	dv/dp for $p < 0.8$ GPa ($\text{cm}^{-1}\text{ GPa}^{-1}$)	dv/dp for $p > 0.8$ GPa ($\text{cm}^{-1}\text{ GPa}^{-1}$)
460	1.12 ± 0.17	0.60 ± 0.04
510	-0.04 ± 0.03	0.47 ± 0.04
535	1.50 ± 0.18	1.95 ± 0.05
565	1.34 ± 0.37	2.11 ± 0.06
577	-0.20 ± 0.07	-0.30 ± 0.02
642	0.19 ± 0.06	0.21 ± 0.01
673	-0.29 ± 0.01	-0.45 ± 0.02
742	-1.11 ± 0.17	-0.38 ± 0.03
1134	2.77 ± 0.35	2.51 ± 0.07
1251	3.34 ± 0.75	2.30 ± 0.09

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